BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

Translated from French by the Ralph McElroy Translation Company
910 West Avenue, Austin, Texas 78701 USA

Code: 1505-77295

INTERNATIONAL PATENT OFFICE
WORLD ORGANIZATION FOR INTELLECTUAL PROPERTY
International patent published on
the basis of the Patent Cooperation Treaty (PCT)
INTERNATIONAL PUBLICATION NO. WO 98/31329 A1

International Patent Classification[6]:	A 61 K 7/06 7/032
International Filing No.:	PCT/FR98/00080
International Filing Date:	January 16, 1998
International Publication Date:	July 23, 1998
Priority	
Date:	January 20, 1997
No.:	97/00545
Country:	FR

COSMETIC COMPOSITION CONTAINING AS COATING AGENT FOR KERATINOUS FIBERS A FILM-FORMING MIXTURE CONSISTING OF POLYMER PARTICLES CAPABLE OF BEING FILM-FORMED AND PARTICLES NOT CAPABLE OF BEING FILM-FORMED

Patent Applicant (for all the Designated Contracting States except US):	L'OREAL (FR/FR) 14, rue Royale F-75008 Paris (FR)
Inventor; and Inventor/Applicant (only for US):	Nathalie Mougin (FR/FR) 28, rue Merlin F-75011 Paris (FR)
Representative:	Laurent Miszputen L'Oréal/DPI 90, rue du Général-Roguet F-92583 Clichy Cedex (FR)

Designated Contracting States: CA, CN, JP, KR, US, European Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report

FOR INFORMATION ONLY

Codes for the identification of PCT contract states on the cover sheets of the documents that publish the international applications in accordance with the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia-Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldavia
MG	Madagascar
MK	Macedonia (former Yugoslavian Republic of Macedonia)
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Vietnam
YU	Yugoslavia
ZW	Zimbabwe

Abstract

The invention concerns cosmetic or dermatological compositions containing in a cosmetically acceptable aqueous medium, as coating agent for keratinous fibres, 15 to 60 % by weight of dry extract of a film-forming mixture consisting of: (A) at least an aqueous dispersion of polymer particles capable of being film-formed on their own or film-formed in the presence of at least one plasticizer; the glass temperature Tg of the polymer or of the polymer/plasticizer being not more than 25 °C; and (B) at least an aqueous dispersion of spherical and anisotropic particles not capable of being film-formed, for forming a percolation network dispersed in the matrix of the film formed from the particles capable of being film-formed and optionally from the plasticizer; said particles not capable of being film-formed are different from the pigments and are present in said film-forming mixture in concentrations ranging from 20 to 90 % by volume when they are spherical and in concentrations ranging from 10 to 80 % by volume when they are anisotropic. These compositions can be used as base for make-up products for eyelashes and eyebrows or as base for capillary products for hair styling and/or hair care.

The present invention relates to a cosmetic or dermatological composition comprising, in a cosmetically acceptable aqueous medium, as a coating agent for keratinous fibers, a film-forming mixture consisting of polymer particles capable of being film-formed and of rigid nonfilm-forming particles, and to their uses in the field of cosmetics or dermopharmacy, notably in eyelash and eyebrow makeup products and in products for hair styling and/or hair care.

There are two known traditional formulations of mascaras, namely the so-called "cream" aqueous mascaras in the form of an emulsion of wax in water and the so-called "waterproof" mascaras, which are anhydrous or have a low water content, and which are dispersions of waxes in oils.

The conventional cream mascaras generally distribute themselves well along the eyelash and they form a homogeneous deposit along the eyelash, producing a satisfactory lengthening of the eyelash. However, they present the drawback of having little resistance to water and to ambient humidity (rain, tears, baths, etc) and they present poor mechanical properties, such as resistance to dry friction (wiping of the hands over the eyelids).

The conventional waterproof mascaras have a very high resistance to water and to ambient humidity but they present poor properties with regard to the deposition and the distribution of a product along the eyelash, the dyeing of the eyelash and the mechanical properties, and moreover, they require the use of specific makeup removal products based on oil because of their high remanence in water.

To overcome these different technical problems, it has been proposed for several years to add to the traditional mascara formulations, dispersions of polymer particles that are capable of being film-formed, as an agent which allows improving the resistance to water, or facilitating the makeup removal, or improving the properties pertaining to the makeup of the eyelashes. These formulations containing waxes, however, lead to mechanical properties that are still insufficient.

One of the objectives of the present invention is to prepare a novel formulation of aqueous mascaras using, as an agent for coating eyelashes, an aqueous dispersion of polymer

particles that is capable of being film-formed, optionally in the presence of a plasticizer, and provides a solution for the above-mentioned drawbacks.

The applicant has observed that an aqueous mascara composition containing an aqueous suspension of pigments and using, as a coating agent for the eyelashes, a suspension of film-forming polymer particles, optionally in the presence of a plasticizer, led to a heterogeneous, discontinuous and undesirable deposit on the eyelash. The addition of surfactants to the formulation of mascara for the purpose of lowering its surface tension to a value which is less than the surface tension of an eyelash does not allow the elimination of this phenomenon.

Therefore, it is desirable to conceive novel mascara formulations based on film-forming polymer particles, and pigments in suspension that allow an appreciable attenuation of this phenomenon, and even its elimination.

The capillaire products for hair styling of the prior art which use, as principal or auxiliary agent for coating hair, an aqueous dispersion of film-forming polymer particles, optionally in the presence of plasticizers, also tend to lead, after deposition and drying, to a heterogeneous and discontinuous sheathing of the hair.

Another objective of the present invention is to prepare capillaire formulations for hair styling and/or hair care containing, as a principal agent for coating eyelashes [sic], an aqueous suspension of film-forming polymer particles, optionally in the presence of a plasticizer, and which allows an appreciable attenuation of this phenomenon, and even its complete elimination.

The applicant has discovered, surprisingly, that by combining with certain types of aqueous dispersions of film-forming polymer particles, certain particles in particular proportions which will be described below in the description, one can prepare formulations of aqueous mascaras containing a composite film producing material that not only allows solving all the problems specific to mascaras, as mentioned above, but that also allows the obtaining of a homogeneous and continuous sheathing of the eyelash.

The applicant also has discovered that this particular combination led to the formation of an original composite material constituting an agent for coating hair, which has simultaneously good cosmetic properties, notably with respect to feel to the touch and untangling, good film producing properties, satisfactory mechanical properties for hair care, and which allowed the obtaining of a better sheathing of the hair.

The cosmetic or dermatological compositions according to the invention are characterized by the fact that they contain in a cosmetically acceptable aqueous medium, as an agent for coating keratinous fibers, 15-60 wt%, by dry extract, of a film producing mixture consisting of:

(A) at least an aqueous dispersion of polymer particles film-forming by themselves, or film-forming in the presence of at least a plasticizing agent; the temperature Tg of vitreous

transition of the polymer and the polymer/plasticizer mixture being less than or equal to 25°C; and

(B) at least an aqueous dispersion of nonfilm-forming particles, which may be spherical or anisotropic, capable of forming a percolation network in the matrix of the film formed from the film-forming particles, and, optionally, the plasticizer;

said nonfilm-forming particles are different from pigments and they are present in said film-forming mixture in concentrations of 20-90 vol% when they are spherical and concentrations of 10-80 vol% when they are anisotropic.

The term "network of percolation in the matrix of the polymer that has been film-formed," denotes the network formed by the film-producing particles by interconnection and formation of aggregates, dispersed inside the entire matrix of polymer film starting at a certain threshold fraction by volume of said particles in the film-producing mixture of the invention. Below this threshold, the nonfilm-forming particles are not percolating and they are distributed randomly in the matrix of the polymer film. This type of behavior is described in the article by Nicole Alberola, Corinne Bas and Patrice Mele, C. R. Sci. Paris, Vol. 319, Series II, pp. 1129-1134, 1994.

To simultaneously obtain, along with a rapid film formation, a good adhesion to the keratinous fiber, a good mechanical resistance, and a good resistance to dry friction of the composite material deposited on the keratinous support after drying without gluing effect, the nonfilm-forming particles according to the invention must be present in the mixture consisting of the film-forming polymer particles and the particles that cannot be film-formed in concentrations of 20-90 vol% and preferably 20-80 vol% when they are spherical and in concentrations of 10-80 vol% and preferably 10-70 vol% when they are anisotropic.

When the fraction by volume of the nonfilm-forming particles in the film-forming mixture is below the minimum fractions by volume indicated above, the network of percolation in the film-formed matrix of polymer no longer forms, and the mechanical properties of the sheathing of the keratinous fibers are no longer satisfactory. One also obtains, after drying, in this case a deposit on the fiber with gluing character. When the fraction by volume of particles that cannot be film-formed in the film-forming mixture is above the maximum fractions by volume indicated above, one observes a poor film formation of the composite material on the fiber.

The film-forming polymer particles are chosen from all the known polymer types in cosmetics that are capable of forming, in the presence or the absence of plasticizers, a film-forming material having a vitreous transition temperature Tg less than or equal to 25°C, and more advantageously from –50 to 25°C.

To obtain a more rapid film formation and a better adhesion of the composite material resulting from the combination of the invention on the keratinous support (eyelash, eyebrow or hair), the vitreous transition temperature Tg of the polymer or of the polymer/plasticizer mixture must preferably be less than or equal to 10°C.

Among the polymers forming the film-forming particles, one can mention, for example, the polymers with ethylene unsaturation, such as polyacrylics, polyvinyls, polyolefins; polycondensates such as polyurethanes, polyesters, polyamides, polyureas; natural or modified natural polymers such as certain cellulose ethers, such as the product Aquacoat marketed by Seppic (ethylcellulose pseudo-latex) or certain cellulose esters, such as the product CAB –SU 160 marketed by Eastman (partially neutralized cellulose acetobutyrate succinate latex).

To obtain a better elimination by shampooing in the context of capillaire compositions, or a better makeup removal by conventional solutions of surfactants in the context of products for the makeup of eyelashes or eyebrows while preserving a good remanence in water and ambient humidity, it is preferred to use amphoteric film-forming polymers containing monomers that carry amphoteric groups, such as betaine monomers or anionic polymers containing monomers that carry ionized or ionizable anionic groups, in particular carboxylic acid groups and/or sulfonic acid groups and/or phosphoric acid groups. The proportion of amphoteric or anionic monomer in general varies from 2 - 15 wt% with reference to the total weight of the monomers constituting the film-forming polymer.

The betaine or acidic groups are preferably partially or completely neutralized in such a manner that the final pH of the mixture formed by the aqueous dispersion of film-forming particles and of the aqueous dispersion of rigid nonfilm-forming particles must be between 4 and 8, and more advantageously between 6 and 7.5.

The neutralizing agents are preferably chosen from the mineral bases, such as sodium hydroxide or potash, or from the amino alcohols chosen, for example, from the group consisting of 2-amino-2-methyl-1-propanol (AMP), triethanolamine, triisopropanolamine (TIPA), monoethanolamine, tri[(2-hydroxy)-1-propylamine, 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-hydroxymethyl-1,3-propanediol.

The molecular weight, measured by steric exclusion chromatography, of these film-forming polymers is generally less than or equal to 500,000.

The particles according to the invention that are nonfilm-forming can be of any type. They can be mineral or organic, spherical or anisotropic (for example, in the form of ellipsoids, disks, plates, sticks, or fibrils). They differ from the pigments that are usually used in the cosmetic or dermatological compositions.

In the entire description, the term pigment denotes any substance (or materials), natural or synthetic, consisting of fine particles that are insoluble in their medium of use and whose

principal function consists in imparting to the keratinous substances dyeing or covering properties.

Among the dyeing pigments, one can mention, for example, the mineral pigments, such as the zirconium, cerium, zinc or chromium oxides, titanium dioxide, iron oxides, organic pigments such as carbon black or D & C red 36. Among the covering pigments, one can mention kaolin, talc, titanium oxide, zirconium oxide, barium sulfate, magnesium carbonate, or equivalents thereof.

When they are spherical, the mean size of the nonfilm forming particles of the invention is preferably less than or equal to 1 μm, and more advantageously less than or equal to 600 nm. When they are anisotropic, the largest size is preferably less than or equal to 30 μm, and more advantageously less than or equal to 10 μm.

The nonfilm-forming particles of the organic type used according to the present invention are preferably polymer particles having a vitreous transition temperature T'g larger than or equal to 50°C, and more advantageously larger than 70°C.

Among the usable spherical mineral nonfilm-forming particles, one can mention, for example, the silicas. Among the usable anisotropic mineral nonfilm-forming particles, one can mention, for example, the clays (platelets), such as the montmorillonites, the laponites, the bentonites, in particular the commercial product Optigel WA sold by Sud Chimie, the mineral microfibrils, such as certain titanates, such as the commercial product Fybex, sold by duPont de Nemours, and silicon carbide particles.

Among the usable spherical organic nonfilm-forming particles, the following are mentioned:

- polymers with ethylene unsaturation, such as polyacrylics or polyvinyl having a vitreous transition temperature larger than or equal to 50°C;

- the polycondensates such as polyurethanes or polyureas having a vitreous transition temperature larger than or equal to 50°C.

The nonfilm-forming particles of the invention preferably consist of spherical particles of crosslinked polymer.

Among the polymers forming the film-forming particles, one can mention, for example, the, preferably crosslinked, polymers or copolymers obtained by polymerization or copolymerization of a monomer or a mixture of monomers chosen from the group consisting of linear, cyclic, or branched C_1-C_{10} alkyl acrylates or methacrylates, such as methyl methyl methacrylate, tertbutyl methacrylate, cyclohexyl methacrylate, isobornyl acrylate or methacrylate; styrene; vinyltoluene; vinyl chloride, vinyl benzoate or vinyl tertbutyl benzoate; acrylic acid, methacrylic acid.

Particularly preferred polymers are crosslinked copolymers of at least one linear, cyclic, or branched C_1-C_8 alkyl methacrylate and acrylic acid and/or methacrylic acid.

The crosslinking agents are preferably chosen from those routinely used in radical polymerization. One can mention, for example, the ethylene glycol, polyethylene glycol, and propylene glycol diacrylates or dimethacrylates, vinyl benzene, pentaerythritol di- or trimethacrylate; alkylenediol diacrylates or dimethyl acrylates, such as hexanediol dimethacrylate. They are used in quantities that range, preferably, from 0.1 - 50 wt% with reference to the weight of the monomers constituting the nonfilm-forming polymer.

To obtain a better elimination by shampoos (aqueous solution of surfactants) in the context of capillaire compositions or a better makeup removal by means of standard solutions of surfactants in the context of eyelash or eyebrow makeup products, while preserving a good remanence in water or in ambient humidity, one can also use nonfilm-forming particles consisting of amphoteric polymer containing monomers that are carriers of amphoteric groups, such as betaine monomers or nonfilm-forming particles consisting of anionic polymers containing monomers that are carriers of ionized or ionizable anionic groups, in particular carboxylic acid groups and/or sulfonic acid groups and/or phosphoric acid groups. The proportion of amphoteric or anionic monomer generally varies from 2 - 15 wt% with reference to the total weight of the monomers constituting the nonfilm-forming polymer.

The betaine or acid groups are preferably partially or completely neutralized in such a manner that the final pH of the mixture formed by the aqueous dispersion of film-forming particles and of the aqueous dispersion of nonfilm-forming particles is between 4 and 8 and, more advantageously, between 6 and 7.5.

It is preferred that the mixture consisting of the film-forming particles and the rigid nonfilm-forming particles is present, in terms of dry extract in the compositions of the invention in concentrations of 25-60 wt% with reference to the total weight of the composition.

The dispersions of film-forming or nonfilm-forming polymer particles according to the invention can be obtained by batch emulsion polymerization, according to a method comprising:

a) the preparation of a bottom portion in the reactor containing water, possibly a buffer and an emulsifier;

b) the addition in the bottom portion, at ambient temperature, of the monomers;

c) the emulsification of the monomers;

d) the heating of the reaction medium to the polymerization temperature in the presence of a radical primer.

One can also operate in a semi-batch mode using a bottom portion which contains only the aqueous part, a small part of the mixture of monomers, and a part of the initiator. One then heats to the reaction temperature and one performs a simultaneous double pouring of the

remainder of the mixture of monomers and of the remainder of initiator dissolved in a quantity of water.

The compositions according to the invention can optionally also contain a plasticizer to improve the mechanical properties, the cosmetic properties, and the adhesion on the keratinous fibers of the composite material deposited after application and drying.

Among the plasticizers that can be used according to the invention, one can mention:

- the Carbitols of the Union Carbide Company, namely Carbitol, or diethylene glycol ethyl ether, the methyl Carbitol or diethylene glycol methyl ether, the butyl Carbitol or diethylene glycol butyl ether or hexyl Carbitol or diethylene glycol hexyl ether,

- the Cellosolves from the Company Union Carbide, namely Cellosolve or ethylene glycol ethyl ether, the butyl Cellosolve or ethylene glycol butyl ether, the hexyl Cellosolve or ethylene glycol hexyl ether,

- the derivatives of propylene glycol and, in particular, propylene glycol phenyl ether, propylene glycol diacetate, dipropylene glycol butyl ether, tripropyplene glycol butyl ether, as well as the Dowanols from the company Dow Chemical, namely Dowanol PM or propylene glycol methyl ether, Dowanol DPM or dipropylene glycol methyl ether, and Dowanol TPM or tripropylene glycol methyl ether.

One can also mention:

- diethylene glycol methyl ether or Dowanol DM from the company Dow Chemical,

- ricinus oil oxyethylenated with 40 mol ethylene oxide, such as the one sold by the company Rhône Poulenc under the name of "Mulgofen LE-719,"

- benzyl alcohol,

- the triethyl citrate sold by the company Pfizer under the name of "Citroflex-2,"

- 1,3-butylene glycol,

- the diethyl, dibutyl, and diisopropyl phthalates and adipates,

- the diethyl and dibutyl tartrates,

- the diethyl, dibutyl and 2-diethylhexyl phosphates, and

- the glycerol esters, such as glycerol diacetate (diacetine) and glycerol triacetate (triacetine).

The plasticizer is present in a proportion ranging, preferably, from 0 - 20 wt% with reference to the weight of the mixture consisting of the film-forming polymer particles and the nonfilm-forming particles. This proportion varies depending on the intended application.

The cosmetically acceptable aqueous medium of the compositions of the invention preferably consists of water or a mixture of water and at least one cosmetically acceptable solvent compatible with the nonfilm-forming particles and the film-forming particles, such as a monoalcohol, polyalcohol, a glycol ether, acetone or an ester, alone or in the form of a mixture.

It consists, more specifically, of water or of water and of a lower C_{1-4} alcohol, such as ethanol or isopropanol.

The compositions according to the invention as defined above can be used as a base capillaire product for hair dressing and/or care, in particular aerosol lacquers or pump flasks to fix the hair, lotions for perming or brushing, hair styling gels or foams.

The capillaire compositions according to the invention can contain, in addition to the conventional cosmetic additives, such as preservatives, softeners, sequestering agents, perfumes, dyes, viscosity modifying agents, propellants, nacreous agents, hydrating agents, antidandruff agents, antiseborrheic agents, sun screens, hair conditioners, antioxidants, proteins, and vitamins.

The compositions according to the present invention can be used as a base product for the makeup of eyelashes and eyebrows, such as mascara or eyeliner.

The compositions for the makeup of eyelashes and eyebrows generally contain pigments. These pigments can be organic or mineral, or they can also be nacreous pigments. Such pigments are well-known and they are described, in particular, in FR 83-09997 (2.528.699). They can be in the form of a pigment paste, such as the commercial products Cosmenyl sold by the company Hoechst.

The compositions for makeup of eyelashes and eyebrows according to the invention can also comprise at least one conventional additive chosen from a softener, a preservative, a sequestering agent, a perfume, a thickener, an oil, a silicone, a cohesion imparting agent, an alkalinizing or acidifying agent, a filler, anionic surfactants and/or nonionic surfactants.

Another object of the invention consists in the use of the film-forming mixture consisting of:

- the aqueous dispersion of particles of a film-forming polymer as defined above;
- the aqueous dispersion of rigid nonfilm-forming particles as defined above; as coating agent of keratinous fibers in and for the preparation of a cosmetic or dermatological composition.

Another object of the invention consists of the use of said film-forming mixture in and for the preparation of a cosmetic or dermatological composition intended to be applied to keratinous fibers and to form a homogeneous and continuous sheathing of said fibers.

The following examples serve to illustrate the invention without presenting any limiting character.

Example 1: Preparation of a dispersion of rigid acrylic nonfilm-forming polymer particles

Composition of the polymer:

- methyl methacrylate	91 wt%
- methacrylic acid	5 wt%
- ethylene glycol dimethacrylate (crosslinking agent)	4 wt%

Protocol:

In a reactor equipped with a central mechanical stirring device, a thermometer and a coolant, one introduces 100 g ion-exchanged water, 16 g active substance of an alkyl ethoxy sulfate surfactant sold under the name of Abex Jkb by the company Rhone Poulenc and 2.5 g potassium persulfate. The mixture is heated under rapid stirring to a temperature of 80°C.

Simultaneously, one prepares the following two so called "pouring" solutions S_1 and S_2:

Pouring S_1 (solution of monomers):

- Methyl methacrylate	1820 g
- Methacrylic acid	100 g
- Ethylene glycol dimethacrylate (crosslinking agent)	80 g

Pouring S_2:

- Ion-exchanged water	5000 g
- Abex JKB	160 g
- Potassium persulfate	7.5 g

When the aqueous solution in the reactor has reached a temperature of 80°C, one adds 10% of the solution S_1 and one allows the reaction to proceed for 15 min. Then, over a 4-h period, one pours, at a constant flow rate and simultaneously, the remainder of the solution S_1 and the solution S_2. At the end of the two simultaneous additions, one raises the temperature of the reaction medium to 85°C, and one maintains this temperature for 30 min.

One allows the mixture to cool to ambient temperature under stirring. One filters through a nylon sheet.

A dispersion of polymer particles is obtained, which present the following characteristics:

- Mean particle size: 92 nm
- Polydispersity by size of the particles, measured by quasi-elastic scattering of light with an apparatus of the Coulter N4 SD type: <0.1.
- Dry extract in a ventilated oven at 80°C until the weight is constant: 26.6%

Example 2: Preparation of a dispersion of acrylic polymer particles that are capable of being film formed

Composition of a polymer:

- Acrylic acid	10%
- Isobutyl acrylate	70%
- t-Butyl acrylate	20%

Into a reactor equipped with a central mechanical stirring device, a thermometer and a coolant, one introduces 62.5 g ion-exchanged water, 1.24 g of an aqueous solution at 30.4% alkyl ethoxy sulfate surfactant, sold under the name of Abex JKB by the company Rhone Poulenc, and 0.19 g potassium persulfate. One heats the mixtures under rapid stirring to a temperature of 80°C.

Simultaneously, the following two so-called "pouring" solutions S_1 and S_2 are prepared:

Pouring S_1 (solution of monomers):

- Acrylic acid 12.5 g
- Isobutyl acrylate 87.5 g
- t-Butyl acrylate 25 g
- Dodecane thiol 1.25 g

Pouring S_2:

- Ion-exchanged water 312.5 g
- Abex JKB aqueous solution at 30.24% 11.16 g
- Potassium persulfate 0.55 g

When the aqueous solution in the reactor has reached the temperature of 80°C, one adds 10% of the solution S_1 and one allows the reaction to proceed for 15 min. Then, over a 4-h period, one pours, at a constant flow rate and simultaneously, the remainder of the solution S_1 and the solution S_2. At the end of the two simultaneous additions, one raises the temperature of the reaction medium to 85°C and one maintains this temperature for 30 min.

One cools to ambient temperature under stirring. One filters through a nylon sheet.

A dispersion of polymer particles is obtained, presenting the following characteristics:

- Mean particle size: 230 nm
- Polydispersity, by size, of particles measured by quasi-elastic scattering of light with an apparatus of the Coulter N4 SD type: <0.1.
- Dry extract in a ventilated oven at 80°C until the weight is constant: 25%
- Molecular weight at the apex of the steric exclusion chromatography peak: 70,000.
- Vitreous transition temperature measured by DSC: 7°C.

Example 3: Mascara

The following composition A is prepared:

- Dispersion of film-forming polymer particles of Example 2 (concentrated in the rotating evaporator until the dry extract content is 26.6%) 50 wt%
- Dispersion of nonfilm-forming polymer particles of Example 1 (26.6% by dry extract) 50 wt%

- 2-Amino-2-methyl propanol qs pH 7

The composition A obtained is then concentrated in the rotating evaporator until a dry extract content of 40 wt% is obtained.

A mascara formulation is prepared by mixing the following ingredients under magnetic stirring:

- Composition A 93.3 wt%
- Pigment paste sold under the name of Cosmenyl Noir by Hoechst with a 30% active substance content 6.7 wt%

Appearance of the sheathing by the mascara of capillary [hair] fibers or untreated polyamide fibers

One then observes the appearance of the sheathing by the mascara of the invention of an untreated polyamide fiber having a diameter of 100 µm (synthetic model of the eyelash) or of a fiber originating from Dutch blond hair (natural model of the eyelash), said polyamide or capillary fibers having first been washed with a conventional makeup removal solution, such as the commercial product Effacil, marketed by the group L'Oreal, rinsed with water that has been processed by osmosis, and then dried in the open air.

The deposits of the mascara on each fiber are carried out by three consecutive passages of the fiber through a small amount of mascara placed on a glass plate or in a slit conical applicator made of plastic.

Regardless of the fiber, a homogeneous, continuous sheathing with a constant thickness (between 10 and 20 µm, dry) is obtained.

Resistance to water

One then evaluates the resistance to water of the film obtained with the mascara by immersing the fibers sheathed with mascara and then dried for 3 h, in a sufficient quantity of water to cover said fibers. Without stirring, the immersed films swell slightly but they do not separate from the fibers so treated.

Makeup removal:

One also evaluates the makeup removal properties of the mascara of the invention, by immersing the fibers sheathed with mascara and then dried for 24 h in sufficient quantity of a conventional makeup removal solution, such as the commercial product Effacil, to recover said fibers. A slight friction is applied by passing a finger over the immersed film at different times of the immersion. The film separates completely from the capillary fiber after 1 min and from the polyamide fiber after 2 min.

Example 4: Mascara

The following composition B is prepared:

- Dispersion of film-forming polymer particles of Example 2 (26.6% by dry extract content) 30 wt%
- Dispersion of nonfilm-forming polymer particles of Example 1 (26.6% by dry matter content) 70 wt%
- 2-Amino-2-methyl propanol qs pH 8

The composition B obtained is concentrated in the rotating evaporator until a dry extract content of 40 wt% is obtained.

A mascara formulation is prepared by mixing the following ingredients under magnetic stirring:

- Composition B 93.3 wt%
- Pigment paste sold under the name of Cosmenyl Noir by Hoechst at 30% active substance content 6.7 wt%

The same tests as carried out for the mascara of Example 3 are performed. This mascara leads to a homogeneous and continuous sheathing of a capillary fiber and of an untreated polyamide fiber. It presents a good resistance to water and it is easily eliminated by the conventional makeup remover (the film separates completely from the capillary fiber after 1 min and from the polyamide fiber after 2 min).

Example 5: Mascara

A mascara formulation is prepared by mixing the following ingredients under magnetic stirring:

- Composition C 50 wt%
- Dispersion of nonfilm-forming polymer particles of Example 1 (40% by dry extracted content) 50 wt%
- 2-Amino-2-methyl propanol qs pH 7

The same tests as those carried out for the mascara of Example 5 [sic] are performed. This mascara leads to a homogeneous and continuous sheathing on a capillary fiber or an untreated polyamide fiber. It presents a good resistance to water and it is easily eliminated by the conventional makeup remover (the film separates completely from the capillary fiber after 1 min and from the polyamide fiber after 2 min.)

Example 6: Base capillaire product for hair dressing

A base capillaire product for hair dressing is prepared by mixing the following ingredients while stirring:

- Dispersion of anisotropic mineral particles that are not capable of being film-formed sold under the name of *Optigel WA by the company Sud Chimie (dry extract 0.85%) 20 wt%
- Dispersion of film-forming polymer particles of Example 2 (40% by dry extract content) 80 wt%
- 2-Amino-2-methyl propanol qs pH 8

* Smectite bentonite whose largest particle size is 1-5 µm.

One observes the appearance of sheathing of fibers originating from Dutch blond hair, as obtained by this composition under the same conditions of use as for the mascara of Example 3. This composition leads to a homogeneous and continuous sheathing of a capillary fiber.

One also observes the appearance of the sheathing by a composition containing only the dispersion of fiber-forming polymer of Example 2. Such a composition leads to a heterogeneous and discontinuous sheathing of the capillary fiber.

Example 7: Preparation of an aqueous dispersion of particles of an acrylic form-filming polymer

Composition of the polymer (wt%):

- Isobutyl acrylate 97 wt%
- Acrylic acid 3 wt%

In a reactor equipped with a central mechanical stirring device, a condenser, a thermometer, and a nitrogen bubbling tube, one introduces 50 g of ion-exchanged water, 0.3 g the surfactant Abex JKB and 0.154 g potassium persulfate. The mixture is heated under rapid stirring to 80°C.

Simultaneously, the following two so-called "pouring" solutions S_1 and S_2 are prepared:

Pouring S_1 (solution of monomer):

- Isobutyl acrylate 97 g
- Acrylic acid 3 g
- Dodecane thiol 1 g

Pouring S_2:

- Ion-exchanged water 250 g
- ABEX JKB (100% active substance) 2.7 g
- Potassium persulfate 0.446 g

When the bottom portion temperature has reached 80°C, 10% of the monomer mixture of "Pouring No. 1" has been added, and the reaction has been allowed to proceed for 15 min.

One then starts the regular addition over a 4-h period of the remainder of "Pouring No. 1" and simultaneously "Pouring No. 2."

After these 4 h of pouring, the temperature is increased to 85°C, and these conditions are maintained for 30 min. One then allows the reaction medium to return to ambient temperature, and the pH is adjusted to 7 by the addition of 2-amino-2-methyl propanol. One then filters through a nylon fabric. The concentration of the latex is then reduced to 25-40 wt% of dry extract by concentrating in the rotating evaporator.

Determination of the vitreous transition [temperature] TG = -20°C.

Example 8: Preparation of an aqueous dispersion of particles of an acrylic film-forming polymer

Composition of the polymer (wt%):

- Isobutyl acrylate 80 wt%
- Methyl methacrylate 20 wt%

The polymer dispersion was prepared under the same conditions as described in Example 8, without the pH adjustment step, using the following "Pourings" S_1 and S_2.

Pouring S_1 (solution of monomer):

- Isobutyl acrylate 80 g
- Methyl methacrylate 20 g
- Dodecanethiol 1 g

Pouring S_2:

- Ion-exchanged water 250 g
- Abex JKB (100% active substance) 2.7 g
- Potassium persulfate 0.446 g

In this manner a latex with 40% dry extract is obtained.

Determination of the vitreous transition TG = -3°C.

Example 9: Mascara

The extract of the dispersion of Example No. 1 is adjusted to 40 wt% by concentration in the rotating evaporator.

Then, a mixture of the three latexes of Example No. 1 is prepared (particles of a nonfilm-forming polymer), No. 8 and No. 9 (particles of a film-forming polymer) in the following proportions:

- Latex of Example No. 1 (40% extract) 30 g

- Latex of Example No. 8 (40% extract) 35 g
- Latex of Example No. 9 (40% extract) 35 g

The final pH of the mixture is adjusted to 6.5 by the addition of 2-amino-2-methyl propanol.

A mascara formulation is prepared by mixing this combination of three latexes with the pigment paste Cosmenyl Noir of Hoechst, which has already been used in Example No. 3, using the following proportions:

- Mixture of the three latexes 93.3 wt%
- Pigment paste Cosmenyl Noir at 30% of active substance 6.7 wt%

The properties of sheathing imparted by this mascara are observed under the conditions indicated in Example 3. A homogeneous and continuous sheathing having a constant thickness is observed.

* * *

Claims

1. Cosmetic or dermatological composition, characterized by the fact that it contains, in a cosmetically acceptable aqueous medium, as coating agent for keratinous fibers, 15-60 wt% of a dry extract of a film-forming mixture consisting of:

(A) at least an aqueous dispersion of polymer particles film-forming by themselves, or film-formed in the presence of at least a plasticizing agent; the temperature Tg of vitreous transition of the polymer and the polymer/plasticizer mixture being less than or equal to 25°C; and

(B) at least an aqueous dispersion of nonfilm-forming particles, which may be spherical or anisotropic, capable of forming a percolation network in the matrix of the film formed from the film-forming particles, and, optionally, the plasticizer;

said film-forming particles are different from pigments and they are present in said film-forming mixture in concentrations of 20-90 vol% when they are spherical and concentrations of 10-80 vol% when they are anisotropic.

2. Composition according to Claim 1, characterized by the fact that the vitreous transition temperature Tg varies from -50°C to 25°C.

3. Composition according to Claim 1 or 2, characterized by the fact that the vitreous transition temperature Tg is less than or equal to 10°C.

4. Composition according to any one of Claims 1-3, characterized by the fact that the polymers constituting the film-forming particles are chosen from ethylenically unsaturated polymers such as polyacrylics, polyvinyls, polyolefins, polycondensates such as polyurethanes, polyesters, polyamides, polyureas; natural or modified natural polymers.

5. Composition according to any one of Claims 1-4, characterized by the fact that the polymers constituting the film-forming particles are chosen from amphoteric film-forming polymers containing monomers that bear amphoteric groups or anionic polymers containing monomers that bear ionized or ionizable anionic groups.

6. Composition according to Claim 5, characterized by the fact that the proportion of amphoteric monomer or anionic monomer is 2-15 wt% with reference to the total weight of the monomers constituting the polymer that is capable of being film-formed.

7. Composition according to Claim 5 or 6, characterized by the fact that the amphoteric monomers are betainic monomers and by the fact that the anionic monomers contain carboxylic acid groups and/or sulfonic acid groups and/or phosphoric acid groups.

8. Composition according to Claim 7, characterized by the fact that the betainic groups or acids of the, film-forming polymer are partially or completely neutralized in such a manner that the final pH of the mixture consisting of the aqueous dispersion of particles capable of being film-formed and the aqueous dispersion of rigid nonfilm-forming particles is 4-8 and preferably 6-7.5.

9. Composition according to any one of Claims 1-8, characterized by the fact that the polymers constituting the film-forming particles have a molecular weight, measured by steric exclusion chromatography, less than or equal to 500,000.

10. Composition according to any one of Claims 1-9, characterized by the fact that the spherical nonfilm-forming particles have a mean size less than or equal to 1 μm, and preferably less than or equal to 600 nm.

11. Composition according to any one of Claims 1-9, characterized by the fact that the anisotropic nonfilm-forming particles have a maximum size less than or equal to 30 μm and preferably less than or equal to 10 μm.

12. Composition according to any one of Claims 1-11, characterized by the fact that the nonfilm-forming particles of the mineral type are chosen from the group consisting of silicas, clays, titanate microfibrils, and silicon carbides.

13. Composition according to any one of Claims 1-11, characterized by the fact that the nonfilm-forming particles are polymer particles having a vitreous transition temperature T'g less than or equal to 50°C and more particularly higher than 70°C.

14. Composition according to Claim 13, characterized by the fact that the rigid nonfilm-forming particles are spherical particles of crosslinked polymers.

15. Composition according to Claim 14, characterized by the fact that the crosslinking agent is present in proportions of 0.1-50 wt% with reference to the weight of the polymer that is not capable of being film-formed.

16. Composition according to any one of Claims 1-11, 13-15, characterized by the fact that the nonfilm-forming particles are polymer spherical particles chosen from:

- ethylenically unsaturated polymers such as polyacrylics or polyvinyls;

- polycondensates such as polyurethanes or polyureas.

17. Composition according to any one of Claims 1-11, 13-16, characterized by the fact that the polymer constituting the nonfilm-forming particles is chosen from amphoteric groups and polymers that are not capable of being film-formed containing monomers bearing amphoteric or anionic nonfilm-forming polymers containing monomers bearing ionized or ionizable anionic groups.

18. Composition according to Claim 17, characterized by the fact that the proportion of amphoteric monomer or anionic monomer is 2-15 wt% with respect to the total weight of the monomers constituting the nonfilm-forming polymer.

19. Composition according to Claim 17 or 18, characterized by the fact that the amphoteric monomers are betainic monomers and by the fact that the anionic monomers are monomers bearing carboxylic acid groups and/or sulfonic acid groups and/or phosphoric acid groups.

20. Composition according to Claim 20, characterized by the fact that the betainic groups or the acids of film-forming polymer are partially or completely neutralized in such a manner that the final pH of the mixture consisting of the aqueous dispersion of film-forming particles and of the aqueous dispersion of rigid nonfilm-forming particles is 4-8, and preferably 6-7.5.

21. Composition according to any one of Claims 1-20, characterized by the fact that it contains, in addition, a plasticizer in proportions less than or equal to 20 wt% with respect to the total weight of the mixture consisting of particles of polymer that are capable of being film-formed and nonfilm-forming particles.

22. Hair-care product for hair styling and/or hair care, characterized by the fact that it contains at least a composition according to any one of Claims 1-21.

23. Eyebrows and lashes makeup, characterized by the fact that it contains at least a composition according to any one of Claims 1-21.

24. Mascara, characterized by the fact that it contains at least a composition according to any one of Claims 1-21.

25. Utilization of a film-forming mixture consisting of

- an aqueous dispersion of polymer particles capable of being film-formed as defined in any one of Claims 1-21; and

- an aqueous dispersion of nonfilm-forming particles as defined according to any one of Claims 1-21; as agent for coating keratinous fibers in and for the preparation of a cosmetic or dermatological composition.

26. Utilization of a film-forming mixture consisting of

- an aqueous dispersion of particles of a polymer that is capable of being film-formed as defined in any one of Claims 1-21; and

- an aqueous dispersion of rigid nonfilm-forming particles as defined according to any one of Claims 1-21; in and for the preparation of a cosmetic or dermatological composition intended to be applied to keratinous fibers and to form a homogeneous and continuous sheathing of said fibers.

INTERNATIONAL SEARCH REPORT

Interna nal Application No
PCT/FR 98/00080

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06 A61K7/032

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP 0 764 436 A (OREAL) 26 March 1997 see the whole document ---	1-10, 13-26
X	EP 0 288 012 A (KAO CORP) 26 October 1988 see the whole document ---	1,4,5,7, 10, 14-19, 22,25
X	WO 91 12793 A (OREAL) 5 September 1991 see page 1-3 see page 5, line 3-10 see examples 1-10 --- -/--	1,4,12, 22-25

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 April 1998	07/05/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040 Tx. 31 651 epo nl Fax: (+31-70) 340-3016	Sierra Gonzalez, M

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/FR 98/00080

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 238 242 A (MAYBE HOLDING CO) 29 May 1991 see page 1-9; tables 1-3	1,4,5,7, 9-12,15, 16,23-25

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

information on patent family members

Inter ational Application No
PCT/FR 98/00080

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0764436 A	26-03-97	FR 2739022 A	28-03-97
		FR 2739024 A	28-03-97
		CA 2186147 A	22-03-97
		JP 9110631 A	28-04-97
EP 0288012 A	26-10-88	DE 3882162 A	12-08-93
		DE 3882162 T	07-04-94
		ES 2058168 T	01-11-94
		HK 103494 A	07-10-94
		JP 1025713 A	27-01-89
		JP 2539247 B	02-10-96
		PH 25567 A	08-08-91
		SG 112394 G	13-01-95
		US 4957992 A	18-09-90
		US 5039519 A	13-08-91
WO 9112793 A	05-09-91	FR 2659011 A	06-09-91
		AU 635630 B	25-03-93
		AU 7452491 A	18-09-91
		CA 2046600 A	02-09-91
		DE 69101889 D	09-06-94
		DE 69101889 T	22-12-94
		EP 0471054 A	19-02-92
		ES 2052376 T	01-07-94
		JP 2623168 B	25-06-97
		JP 4505469 T	24-09-92
GB 2238242 A	29-05-91	US 5053221 A	01-10-91
		CA 2030289 A	21-05-91
		JP 3209308 A	12-09-91
		MX 172080 B	01-12-93